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Characterizing the transport of natural uranium and its decay product ^{226}Ra, downstream from former mines in France

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Abstract

Surface waters downstream from former uranium mines have been studied in order to characterize U and ^{226}Ra transport and to assess their bioavailability. Filtrations and ultrafiltrations (UF) have been performed (0.45 µm / 0.2 µm / 500 kDa / 100 kDa / 10 kDa) and compared to the *in situ* technique, diffusive gradients in thin films (DGT). One of the study sites, a stream passing through a peatbog located in the vicinity of a former U mine, shows an increase in total U and a slight increase in ^{226}Ra concentrations. While ^{226}Ra is completely dissolved, U is mainly present as particles and colloids, the dissolved fraction reaching only about 5-20%.

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Keywords: uranium; radium; ultrafiltration; diffusive gradient in thin films; DGT; bioavailability; peatbog; uranium mines.

1. Introduction

Between 1945 and 2001, uranium mining in France has led to the production of 76,000 t of uranium (U). Either mined as open pits or underground mines, these former sites also induced large amounts of rock wastes, mine tailings, and mine waters coming from the underground mines. After closure, their decommissioning consisted notably in refilling tunnels and shafts, reshaping rock wastes heaps, dismantling facilities and cleaning up radiological contaminations. Nowadays, besides environmental monitoring, mine waters are collected at their new re-emergence and are subjected to a chemical treatment (typically NaOH, $BaCl_2$, $Al_2(SO_4)_3$) which lowers natural U and ^{226}Ra contents to meet environmental regulations. Downstream from these former mines, the influence of these radionuclides on ecosystems is linked to their bioavailability *i.e.* the fraction immediately available for absorption by

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organisms [1, 2]. This fraction actually depends on their speciation, meaning that it results from the combination of many parameters in the study system, such as water chemistry, nature of solid phases, presence of particles/colloids, presence of organic matter, *etc*. Whereas a norm already exists for measuring bioavailability in sediments [3], several measurement techniques are currently suggested for water. Among those, the *in situ* technique Diffusive Gradient in Thin films (DGT) has been developed to mimic the biological cell membranes [4]. Therefore, in order to control the influence of former U mines on ecosystems, it has become relevant to assess bioavailability as well. This study aims at *(i)* characterizing the transport of natural U and ^{226}Ra, *i.e*. particles, colloids, dissolved species, *(ii)* comparing ultrafiltration (UF) and DGT results and *(iii)* calculating U and ^{226}Ra speciation. Two sites have been studied: Site A is a former mine which underground waters are released in a river after treatment; Site B is a peatbog with a stream, located in the vicinity of another former mine. The latter site is thus likely to contain a significant amount of organic matter that may drastically modify U and ^{226}Ra speciation. This paper focuses specifically on Site B results.

2. Material and Methods

2.1. Sampling

Surface waters of Site B are sampled from upstream to downstream during three sampling campaigns. Physico-chemical parameters such as pH, Eh, dissolved O_2, conductivity, and temperature are measured *in situ*.

2.2. Filtrations and ultrafiltrations (UF)

Filtrations and ultrafiltrations (UF) are performed immediately after sampling. As for filtration, all samples are filtered through 0.45 and 0.2 µm cellulose acetate filters. UF are performed only for HS1, HS2, HS3 and Downstream sampling spots, and for Blank and Post-Blank (with ultrapure water before and after processing samples). UF are done with 500 kDa, 100 kDa and 10 kDa Biomax Millipore© polyethersulfone membranes. Between each sample, filtration and UF devices are rinsed with 2% HNO_3 solution and ultrapure water. All the filtered and ultrafiltered fractions are analyzed for cations, traces, radioactivity, anions and Total Organic Carbon. Samples are acidified down to pH 2 with ultrapure HNO_3 for cations/traces/radioactivity measurements and with ultrapure H_2SO_4 for NH_4^+ analyses. Raw concentrations of U and ^{226}Ra are assessed by analyzing the 0.2 µm filters.

2.3. Diffusive Gradient in Thin films (DGT)

The technique of Diffusive Gradient in Thin Films (DGT) is applied for the determination of the "DGT-labile" dissolved fraction of U, ^{226}Ra, Ba, Al, Fe and Mn in surface waters. DGT is an *in situ* sampling device based on a mass transport of metals through a diffusive gel, respecting the initial *in situ* conditions in aquatic systems. This technique allows a preconcentration of metals on a resin gel in function of the deployment time. U, Ba, Al, Fe and Mn are trapped on Chelex© resin and ^{226}Ra on MnO_2 resin. The device is eluted with HNO_3, and this solution is analyzed by HR-ICP-MS.

2.4. Speciation calculation

Speciation is calculated for water chemistry of the 10 kDa fractions. PhreeqC and Geochemist's Workbench softwares are used with the LLNL database implemented with the set of thermodynamic data of U [5-7] and with the fewer available for Ra [8, 9].

3. Results

In Site B, surface waters of the stream have been sampled from its spring (upstream from the peatbog) to its output from the peat bog. These waters are oxygenated (dissolved O_2 in the range of 8-10 $mg.L^{-1}$), near-neutral (pH ≈ 6), oxidizing (Eh between 120 and 430 mV/SHE) with low conductivity (40-110 $\mu S.cm^{-1}$), indeed "major ions" are in the range of 10^{-4} $mol.L^{-1}$. Figure 1 illustrates the overall increase of U concentrations along the peat bog, whatever the (ultra)filtration thresholds.

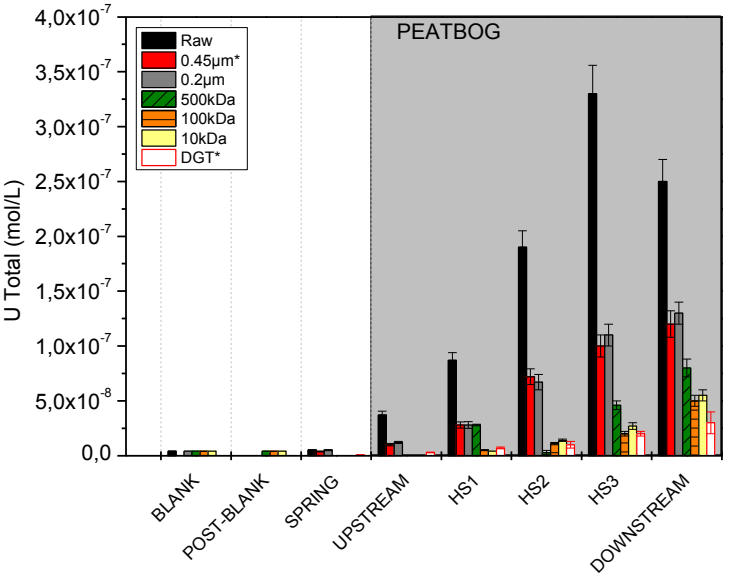

Fig. 1. Total U concentration in raw (>0.2 µm), filtered, ultrafiltered samples and DGT, from the spring to downstream.

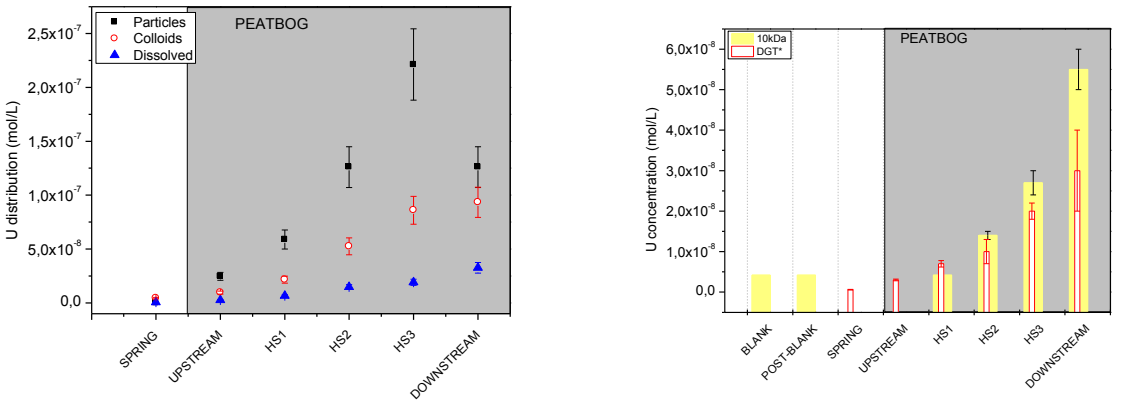

Fig. 2. (a) U distribution between particles, colloids and dissolved fractions; (b) Comparison between dissolved U concentrations measured by 10 kDa ultrafiltration and DGT.

Blank, Post-Blank and Spring samples contain $[U]_{tot.} \leq 5.10^{-9}$ mol.L^{-1}, thus confirming the adequate experimental methodology and the fact that the Spring sampling spot is not influenced by mining activities. Uranium contents in the stream, inside the peatbog area, are significantly different between raw (>0.2 µm), 0.45/0.2 µm, 500 kDa and 100/10 kDa fractions. Figure 2-a shows that the particular concentrations ([Raw]-[0.45/0.2 µm]) increase from Upstream to HS3, representing about 65% of Total U content, then decrease at Downstream, accounting for 45-50%. Colloidal fractions ([0.45/0.2 µm]-[10 kDa] or DGT) and dissolved concentrations present the same trend as well, representing 25-45% and 5-20% respectively. In Figure 2-b, dissolved U concentrations obtained by 10 kDa ultrafiltration and DGT are compared for HS1, HS2, HS3 and Downstream. Both results are equivalent for HS1 and HS2, then DGT results become lower for HS3 and Downstream.
Radium distribution demonstrates that ^{226}Ra is mainly dissolved ($\approx 10^{-14}$ mol.L^{-1}) and increases slightly along the peatbog. Study of Al, Fe, Mn and Ba distribution evidences the presence of Al and Fe colloids.

4. Discussion and conclusion-outlooks

UF and DGT experiments in Site B have shown that Total U concentration increases in the stream along the peatbog from upstream to downstream. This observation is consistent with a release of radionuclides by the peatbog, which (bio)geochemical conditions enables trace metals and radionuclides such as U entrapment [10,11]. Moreover, U is mainly present as particles and colloids, whereas ^{226}Ra is totally dissolved. Uranium behaviour can be correlated to the presence of Al and Fe colloids (alumino-silicates and HFO), yet organic colloids are currently tested as well. Comparing the three sampling campaigns will evidence whether seasonal variations have a significant influence on U and ^{226}Ra mobility.

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